

POLYMERIC BLENDS THAT ADHERE TO POLYESTER

FIELD OF THE INVENTION

5 This invention relates to polymeric blends that have a high adhesion to copolyesters and can be overmolded onto a copolyester insert.

BACKGROUND OF THE INVENTION

10 Injection molding is a common technique employed to prepare a number of polymeric products. It is often necessary to injection mold one polymeric material onto another polymeric object or substrate of a distinct material. This technique is often referred to as overmolding whereby the second or adhesive material is molded onto a first material which is often called an insert. The process can be accomplished in two stages, *i.e.*, using two separate injection molders, or in a single stage whereby a single extruder is employed that is
15 equipped to extrude two different materials.

The ability to overmold one polymeric material onto an insert requires that the second material adhere to the first material, *i.e.*, the insert. And, it is important that the bond between the first material (*i.e.*, the overmold material) and the insert remain while the overmold material cools.

20 Many molded polymeric products are fabricated from thermoplastic copolyesters. Thermoplastic copolyesters include, but are not limited to, polycyclohexalene dimethylene terephthalate that is acid modified (PCTA), polycyclohexalene dimethylene terephthalate that is glycol modified (PCTG), poly(ethylene terephthalate) glycol (PETG), and poly(ethylene terephthalate)
25 (PET). Unfortunately, it is difficult to bond moldable materials to copolyesters. Accordingly, there is a need to develop an overmolding material that will bond to copolyesters.

SUMMARY OF THE INVENTION

30 In general the present invention provides a polymeric blends comprising

from about 2 to about 30 percent by weight thermoplastic polyurethane elastomer, from about 55 to about 145 parts by weight copolyester per 100 parts by weight thermoplastic polyurethane elastomer, from about 400 to about 1,000 parts by weight ethylene vinyl acetate copolymer per 100 parts by weight

thermoplastic polyurethane elastomer, from about 15 to about 85 parts by weight softening agent per 100 parts by weight thermoplastic polyurethane elastomer, and from about 15 to about 85 parts by weight compatibilizing agent per 100 parts by weight thermoplastic polyurethane elastomer.

5 The present invention also includes a polymeric blend comprising from about 6 to about 14 percent by weight thermoplastic polyurethane, from about 6 to about 14 percent by weight copolyester, from about 55 to about 85 percent by weight ethylene vinyl acetate copolymer, from about 2 to about 85 percent by weight styrene-isoprene-styrene block copolymer, and from about 2 to about 8
10 percent by weight maleic anhydride modified polypropylene.

 The present invention further includes a polymeric blend comprising from about 6 to about 14 percent by weight thermoplastic polyurethane, from about 6 to about 14 percent by weight copolyester, from about 55 to about 85 percent by weight ethylene vinyl acetate copolymer, from about 2 to about 85
15 percent by weight styrene-isoprene-styrene block copolymer, and from about 2 to about 8 percent by weight maleic anhydride modified EPDM.

 The polymeric blends of this invention can advantageously be overmolded onto copolyester inserts and remain adhered during the cooling process. Advantageously, the polymeric blends of this invention have a very low
20 shrinkage factor, which is generally less than 1.0%.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

I. General

 The polymeric blends of this invention include a thermoplastic
25 polyurethane elastomer (TPU), an ethylene vinyl acetate copolymer (EVA), and a thermoplastic copolyester. In one embodiment, the polymeric blend includes a TPU, EVA, a copolyester, a softening agent, and a compatibilizer. Other ingredients may likewise be included that are typically found in polymeric blends.

30 II. Thermoplastic Polyurethane

 The TPU component has no limitation in respect of its formulation other than the requirement that it be thermoplastic in nature which means it is prepared from substantially difunctional ingredients, *i.e.*, organic diisocyanates and components being substantially difunctional in active hydrogen containing

groups. However, often times minor proportions of ingredients with functionalities higher than two may be employed. This is particularly true when using extenders such as glycerin, trimethylolpropane, and the like. Accordingly, any of the TPU materials known in the art can be employed in the present blends.

5 For representative teaching on the preparation of TPU materials see Polyurethanes: Chemistry and Technology, Part II, Saunders and Frisch, 1964, pp 767 to 769, Interscience Publishers, New York, N.Y. and Polyurethane Handbook, Edited by G. Oertel 1985, pp 405 to 417, Hanser Publications, distributed in U.S.A. by Macmillan Publishing Co., Inc., New York, N.Y. For particular teaching on
10 various TPU materials and their preparation see U.S. patent publications U.S. Pat. Nos. 2,929,800; 2,948,691; 3,493,634; 3,620,905; 3,642,964; 3,963,679; 4,131,604; 4,169,196; Re 31,671; 4,245,081; 4,371,684; 4,379,904; 4,447,590; 4,523,005; 4,621,113; 4,631,329; and 4,883,837, which are incorporated herein by reference. Similar definitions can be found in U.S. Patent Nos. 6,001,484,
15 5,852,118, and 6,072,003, which are incorporated herein by reference.

The preferred TPU is a polymer prepared from a mixture comprising at least one organic diisocyanate, at least one polymeric diol and at least one difunctional extender. The TPU may be prepared by the prepolymer, quasi-prepolymer, or one-shot methods in accordance with the methods described in the
20 references above.

Any of the organic diisocyanates previously employed in TPU preparation can be employed including blocked or unblocked aromatic, aliphatic, and cycloaliphatic diisocyanates, and mixtures thereof.

Illustrative isocyanates but non-limiting thereof are
25 methylenebis(phenyl isocyanate) including the 4,4'-isomer, the 2,4'-isomer and mixtures thereof, m- and p-phenylene diisocyanates, chlorophenylene diisocyanates, α,α' -xylylene diisocyanate, 2,4- and 2,6-toluene diisocyanate and the mixtures of these latter two isomers which are available commercially, tolidine diisocyanate, hexamethylene diisocyanate, 1,5-naphthalene diisocyanate,
30 isophorone diisocyanate and the like; cycloaliphatic diisocyanates such as methylenebis(cyclohexyl isocyanate) including the 4,4'-isomer, the 2,4'-isomer and mixtures thereof, and all the geometric isomers thereof including trans/trans, cis/trans, cis/cis and mixtures thereof, cyclohexylene diisocyanates (1,2-; 1,3-; or 1,4-), 1-methyl-2,5-cyclohexylene diisocyanate, 1-methyl-2,4-cyclohexylene

diisocyanate, 1-methyl-2,6-cyclohexylene diisocyanate, 4,4'-isopropylidenebis(cyclohexyl isocyanate), 4,4'-diisocyanatodicyclohexyl, and all geometric isomers and mixtures thereof and the like. Also included are the modified forms of methylenebis(phenyl isocyanate). By the latter are meant those forms of methylenebis(phenyl isocyanate) which have been treated to render them stable liquids at ambient temperature (about 20°C.). Such products include those which have been reacted with a minor amount (up to about 0.2 equivalents per equivalent of polyisocyanate) of an aliphatic glycol or a mixture of aliphatic glycols such as the modified methylenebis(phenyl isocyanates) described in U.S. Pat. Nos. 3,394,164; 3,644,457; 3,883,571; 4,031,026; 4,115,429; 4,118,411; and 4,299,347, which are incorporated herein by reference. The modified methylenebis(phenyl isocyanates) also include those which have been treated so as to convert a minor proportion of the diisocyanate to the corresponding carbodiimide which then interacts with further diisocyanate to form uretone-imine groups, the resulting product being a stable liquid at ambient temperatures as described, for example, in U.S. Pat. No. 3,384,653. Mixtures of any of the above-named polyisocyanates can be employed if desired.

Preferred classes of organic diisocyanates include the aromatic and cycloaliphatic diisocyanates. Preferred species within these classes are methylenebis(phenyl isocyanate) including the 4,4'-isomer, the 2,4'-isomer, and mixtures thereof, and methylenebis (cyclohexyl isocyanate) inclusive of the isomers described above.

The polymeric diols which can be used are those conventionally employed in the art for the preparation of TPU elastomers. The polymeric diols are responsible for the formation of soft segments in the resulting polymer and advantageously have molecular weights (number average) falling in the range of 400 to 4,000 and preferably 500 to 3,000. It is not unusual, and, in some cases, it can be advantageous to employ more than one polymeric diol. Exemplary of the diols are polyether diols, polyester diols, hydroxy-terminated polycarbonates, hydroxy-terminated polybutadienes, hydroxy-terminated polybutadiene-acrylonitrile copolymers, hydroxy-terminated copolymers of dialkyl siloxane and alkylene oxides such as ethylene oxide, propylene oxide and the like, and mixtures in which any of the above polyols are employed as major component (greater than

50% w/w) with amino-terminated polyethers and amino-terminated polybutadiene-acrylonitrile copolymers.

Illustrative of polyether polyols are polyoxyethylene glycols, polyoxypropylene glycols which, optionally, have been capped with ethylene oxide residues, random and block copolymers of ethylene oxide and propylene oxide; 5 polytetramethylene glycol, random and block copolymers of tetrahydrofuran and ethylene oxide and/or propylene oxide, and products derived from any of the above reaction with di-functional carboxylic acids or ester derived from said acids in which latter case ester interchange occurs and the esterifying radicals are 10 replaced by polyether glycol radicals. The preferred polyether polyols are random and block copolymers of ethylene and propylene oxide of functionality approximately 2.0 and polytetramethylene glycol polymers of functionality about 2.0.

Illustrative of polyester polyols are those prepared by polymerizing ϵ -caprolactone using an initiator such as ethylene glycol, ethanolamine, and the like; 15 and those prepared by esterification of polycarboxylic acids such as phthalic, terephthalic, succinic, glutaric, adipic, azelaic, and the like; acids with polyhydric alcohols such as ethylene glycol, butanediol, cyclohexanedimethanol, and the like.

Illustrative of the amine-terminated polyethers are the aliphatic 20 primary di-amines structurally derived from polyoxypropylene glycols. Polyether diamines of this type are available from Jefferson Chemical Company under the trademark JEFFAMINE™.

Illustrative of polycarbonates containing hydroxyl groups are those prepared by reaction of diols such as propane-1,3-diol, butane-1,4-diol, hexan-1,6- 25 diol, 1,9-nonanediol, 2-methyloctane-1,8-diol, diethylene glycol, triethylene glycol, dipropylene glycol, and the like, with diarylcarbonates such as diphenylcarbonate or with phosgene.

Illustrative of the silicon-containing polyethers are the copolymers of alkylene oxides with dialkylsiloxanes such as dimethylsiloxane, and the like; see, 30 for example, U.S. Pat. No. 4,057,595 or U.S. Pat. No. 4,631,329 cited supra.

Illustrative of the hydroxy-terminated polybutadiene copolymers are the compounds available under the tradename Poly BD Liquid Resins. Illustrative of the hydroxy- and amine-terminated butadiene/acrylonitrile copolymers are the materials available under the trade name HYCAR hydroxyl-terminated (HT) liquid

polymers and amine-terminated (AT) liquid polymers, respectively. Preferred diols are the polyether and polyester diols set forth above.

The difunctional extender employed can be any of those known in the TPU art disclosed above. Typically the extenders can be aliphatic straight and
5 branched chain diols having from 2 to 10 carbon atoms, inclusive, in the chain. Illustrative of such diols are ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, and the like; 1,4-cyclohexanedimethanol; hydroquinonebis-(hydroxyethyl)ether, cyclohexylenediols (1,4-,1,3-, and 1,2-isomers), isopropylidenebis(cyclohexanols); diethylene glycol,
10 dipropylene glycol, ethanolamine, N-methyl-diethanolamine, and the like; and mixtures of any of the above. As noted previously, in some cases minor proportions (less than about 20 equivalent percent) of the difunctional extender may be replaced by trifunctional extenders without detracting from the thermoplasticity of the resulting TPU; illustrative of such extenders are glycerol,
15 trimethylolpropane, and the like.

While any of the diol extenders described and exemplified above can be employed alone, or in admixture, it is preferred to use 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, ethylene glycol, and diethylene glycol, either alone or in admixture with each other or with one or more
20 aliphatic diols previously named. Particularly preferred diols are 1,4-butanediol, 1,6-hexanediol, and 1,4-cyclohexanedimethanol.

The equivalent proportions of polymeric diol to said extender can vary considerably depending on the desired hardness for the TPU product. Generally speaking, the proportions fall within the respective range of from about 1:1 to
25 about 1:20, preferably from about 1:2 to about 1:10. At the same time the overall ratio of isocyanate equivalents to equivalents of active hydrogen containing materials is within the range of 0.90:1 to 1.10:1, and preferably, 0.95:1 to 1.05:1.

The TPU's can be prepared by conventional methods which are known to the artisan, for instance from U.S. Pat. No. 4,883,837 and the further references
30 cited therein, which are incorporated herein by reference.

TPUs are commercially available. Particularly preferred TPUs include those available under the tradename PELLETHANE™, such as PELLETHANE™ 1000-85A (Dow; Midland, Michigan).

III. Copolyester

Polyesters are condensation polymers characterized by the presence of carboxylate ester groups distributed either regularly or randomly along the repeating units of their main chains. Linear homo- and copolyesters are derived from self-polycondensation of hydroxycarboxylic acids, the polycondensation of dicarboxylic acids with dihydroxy compounds or by ring-opening polymerization of cyclic esters. Included are homopolymers, copolymers and mixed polyesters, as well as block or graft copolymers. The linear polyesters may be classified as aliphatic, partly aromatic or aromatic (polyarylate) polyesters, and have a wide range of properties. Included are high molecular weight, crystalline, thermoplastic polyesters which have high heat-distortion temperatures, good mechanical strength and toughness, and are easily fabricated. Useful materials are the polyalkylene terephthalates obtained from aliphatic glycols and aromatic dicarboxylic acids or esters, particularly polyethylene terephthalate (PET) and polybutylene terephthalate (PBT), also known as polytetramethylene terephthalate.

Linear thermoplastic polyester resins having a softening point above 50°C are satisfactory; polyesters having a softening or melting point above 100°C are preferred; and polyesters having a softening or melting point between 160° and 280°C are most preferred. The polyester preferably has a weight average molecular weight (M_w) between about 15,000 and about 130,000 with a M_w from about 20,000 to about 80,000 being most preferred.

Also useful are the thermoplastic polyester elastomers (A), which is a polyester block copolymer and has, in the polymer chain, (A-1) a high-melting crystalline segment composed mainly of an aromatic polyester unit and (A-2) a low-melting polymer segment composed mainly of an aliphatic polyether unit and/or an aliphatic polyester unit.

The aromatic polyester unit in the high-melting crystalline segment (A-1) (which is a hard segment) is derived from an acid component and a glycol component. The acid component is substantially terephthalic acid and/or 2,6-naphthalenedicarboxylic acid.

As the acid component, there may be used, in combination with terephthalic acid and/or 2,6-naphthalenedicarboxylic acid, a small amount of

other aromatic dicarboxylic acid (*e.g.*, isophthalic acid) or an aliphatic dicarboxylic acid (*e.g.*, adipic acid, sebacic acid, cyclohexane-1,4-dicarboxylic acid, dimer acid).

5 The glycol component constituting the aromatic polyester unit is a glycol of 2-12 carbon atoms, such as ethylene glycol, propylene glycol, tetramethylene glycol, neopentyl glycol, hexanediol, decanediol or the like. The lower limit of the melting point of the high-melting crystalline segment (A-1) is generally 150°C or more, preferably 170°C, more preferably 190°C or more.

10 The aliphatic polyether unit in the low-melting polymer segment (A-2) (which is a soft segment) is derived from a polyalkylene glycol. The polyalkylene glycol is, for example, polyethylene glycol, polypropylene glycol, polytetramethylene glycol or polyethylene glycol-polypropylene glycol block copolymer. Of these, polytetramethylene glycol is particularly preferable.

15 These glycols have a carbon atom number: oxygen atom number ratio of 2 to 4.5, and can be used alone or in admixture.

The aliphatic polyester unit, which is another unit in the low-melting polymer segment (A-2), is derived from an aliphatic dicarboxylic acid as a main acid component and a glycol. The aliphatic dicarboxylic acid as a main acid component is, for example, succinic acid, adipic acid, sebacic acid or 20 decanedicarboxylic acid. The aliphatic dicarboxylic acid may be used in combination with a small amount of an aromatic dicarboxylic acid (*e.g.*, isophthalic acid).

25 The glycol component constituting the aliphatic polyester unit is a glycol of 2-12 carbon atoms. Its specific examples are the same as those mentioned for the glycol component constituting the aromatic polyester unit of the high-melting crystalline segment (A-1).

The aliphatic polyester unit is obtained by polycondensing the above aliphatic dicarboxylic acid and the above glycol by an ordinary process. It may be a homopolyester, a copolyester, or a polylactone (*e.g.*, a poly- ϵ -caprolactone) 30 obtained by subjecting a cyclic lactone to ring-opening polymerization. The upper limit of the melting point of the aliphatic polyester unit is not critical, though it is preferably 130°C or less, particularly preferably 100°C or less.

The molecular weight of the low-melting polymer segment (A-2) is usually 400-6,000.

The weight ratio of the high-melting crystalline segment (A-1) to the low-melting polymer segment (A-2) in the thermoplastic polyester elastomer (A) is preferably 95/5-5/95, more preferably 70/30-30/70.

5 As the thermoplastic polyester elastomer (A), an elastomer having a softening point of 100°C or more is particularly appropriate.

The polyester block copolymer which is used particularly preferably as the thermoplastic polyester elastomer (A), is derived from a polytetramethylene terephthalate or a polytrimethylene terephthalate-2,6-naphthalate as the high-melting crystalline sequent (A-1) and an aliphatic polyether such as
10 polytetramethylene glycol or the like or an aliphatic polyester such as polytetramethylene adipate, poly-ε-caprolactone or the like as the low-melting polymer sequent (A-2). The polyester block copolymer may contain, as part of the dicarboxylic acid and the glycol, polyfunctional components such as polycarboxylic acid, polyfunctional hydroxy compound, hydroxy acid and the like.
15 The polyfunctional components are used in the copolymer in amounts of 3 mole % or less and exhibit a high thickening effect. The polyfunctional components include, for example, trimetallitic acid, trimesic acid, pyromellitic acid, benzophenonetetracarboxylic acid, glycerine, pentaerythritol, and their esters and anhydrides.

20 The thermoplastic polyester elastomer (A) can be produced by an ordinary polymerization process. Preferable processes include a process which comprise heating an aromatic di-carboxylic acid or a dimethyl ester thereof and a low-melting sequent-formable diol at about 150-260°C in the presence of a catalyst to subject them to esterification reaction or ester exchange reaction and
25 then subjecting the reaction product to polycondensation reaction under vacuum while removing the excessive low-molecular diol to obtain a thermoplastic elastomer; a process which comprises a high-melting polyester sequent-formable prepolymer and a low-melting polymer segment-formable prepolymer both prepared in advance, with a bifunctional chain extender reactive with the terminal
30 groups of the prepolymers, subjecting the prepolymers and the chain extender to reaction and keeping the system under high vacuum to remove volatile components to obtain a thermoplastic polyester elastomer; a process which comprises heat-mixing

a high-melting polyester of high polymerization degree with a lactone with heating to subject them to ring-opening polymerization of lactone and ester exchange reaction simultaneously to obtain a thermoplastic polyester elastomer, and processes similar thereto.

5 Particularly useful copolyesters include those available under the tradename EASTAR™ (Eastman; Tennessee). For example, PCTA is available under the tradename BRO03, PCTG is available under the tradename DN004, PETG is available under the tradename GN007, and PET is available under the tradename EN058.

10 **III. Ethylene Vinyl Acetate (EVA)**

Conventional ethylene vinyl acetate copolymers may be employed in practicing the present invention.

A. Characteristics

15 The preferred ethylene vinyl acetate copolymers (EVAs) will include a vinyl acetate concentration of from about 6.5 to about 35 percent by weight, more preferably from about 15 to about 33 percent by weight, and even more preferably from about 25 to about 31 percent by weight.

B. Physical Properties

20 The preferred ethylene vinyl acetate copolymers have a density from about 0.940 to about 0.965 g/cm³, and more preferably from about 0.950 to about 0.960 g/cm³. Furthermore, the preferred ethylene vinyl acetate copolymers will have a melt flow index from about 20 to about 40 g/10 min., more preferably from about 25 to about 35 g/10 min, and still more preferably from about 27 to about 32 g/10 min, as per ASTM D-1238.

25 **C. Mechanical Properties**

The preferred ethylene vinyl acetate copolymers will have a Shore A hardness of from about 45 to about 80, and more preferably from about 55 to about 75.

D. Commercial Source

30 Useful ethylene vinyl acetate copolymers can be obtained under the tradenames LD 740, LD 755, LD 761, LD 767, LD 768, LD 782, LD 783, MV 02528, UL 7720, UL 7740, UL 7750, LD 7760, UL 7765, UL 7840C, and UL 8705 (ExxonMobil; Houston, Texas)

V. Softening Agents

A. General

Various softening agents can be employed to soften the polymeric blends of this invention. Exemplary softening agents include elastomeric copolymers such as terpolymers of ethylene, α -olefins, and optionally diene monomers as described in U.S. Patent Nos. 6,433,090 and 6,437,030, which are incorporated herein by reference, thermoplastic vulcanizates, and thermoplastic elastomer copolymers. Preferably, the polymeric blends of this invention will include both a thermoplastic vulcanizate and a thermoplastic elastomer copolymer.

B. Thermoplastic Vulcanizate

Thermoplastic vulcanizates (TPVs) are thermoplastic elastomers that include polymeric blends of partially or fully cured ethylene-propylene-diene terpolymer dispersed within a polypropylene matrix. These thermoplastic vulcanizates are described in U.S. Patent Nos. 4,130,534, 4,141,863, 4,427,049, 4,130,535, and 4,311,628, which are incorporated herein by reference. These thermoplastic vulcanizates are available under the tradename SANTOPRENE™ (Advanced Elastomer Systems; Akron, Ohio). The preferred SANTOPRENE™ is SANTOPRENE™ 101, 201, 211 171, or 271, which can be obtained with a Shore A of 55 to 73. These TPVs include about 12 to about 18 percent by weight polypropylene, based upon the entire weight of the TPV.

C. Thermoplastic Elastomer Copolymer

The thermoplastic elastomer copolymer is preferably a block copolymer that includes at least one rubbery block and at least one thermoplastic block. Preferably, the copolymer is a triblock that includes at least two thermoplastic blocks attached to opposite ends of a rubber block. The molecular structure of the copolymers may be straight-chain, branched-chained, radial, or types and combinations thereof.

These copolymers preferably have a number average molecular weight (M_n) of from about 100,000 to about 1,000,000, preferably from about 125,000 to about 800,000, and more preferably from about 150,000 to about 500,000. The molecular weight distribution ratio (M_w/M_n) is preferably 10 or less.

Useful thermoplastic elastomer copolymers include, but are not limited to, styrene/butadiene rubber (SBR), styrene/isoprene rubber (SIR),

styrene/isoprene/butadiene rubber (SIBR), styrene-butadiene-styrene block copolymer (SBS), hydrogenated styrene-butadiene-styrene block copolymer (SEBS), hydrogenated styrene-butadiene block copolymer (SEB), styrene-isoprene-styrene block copolymer (SIS), styrene-isoprene block copolymer (SI),
5 hydrogenated styrene-isoprene block copolymer (SEP), hydrogenated styrene-isoprene-styrene block copolymer (SEPS), styrene-ethylene/butylene-ethylene block copolymer (SEBE), styrene-ethylene-styrene block copolymer (SES), ethylene-ethylene/butylene block copolymer (EEB), ethylene-ethylene/butylene/styrene block copolymer (hydrogenated BR-SBR block
10 copolymer), styrene-ethylene/butylene-ethylene block copolymer (SEBE), ethylene-ethylene/butylene-ethylene block copolymer (EEBE) and mixtures thereof. Preferred copolymers include hydrogenated styrene-butadiene-styrene block copolymer (SEBS), and hydrogenated styrene-isoprene-styrene block copolymer (SEPS).

15 The preferred thermoplastic elastomer copolymer is a styrene-isoprene-styrene block copolymer produced via anionic polymerization and available under the tradename VECTOR™ 4111 (Dexco Polymers; Houston, Texas). This particular thermoplastic block copolymer is a linear, pure SIS triblock copolymer with a narrow molecular weight distribution, low styrene, low modulus
20 copolymer. Namely, the copolymer has about 18 percent by weight styrene content, less than 1.0 percent by weight diblock content, and an MFR (200°C/5kg) of about 12 g/10 min per ASTM D-1238.

VI. Compatibilizing Agent

A. General

25 Various compatibilizing agents can be employed to compatibilize the various constituents of the polymeric blends of this invention. Preferred compatibilizing agents include modified or functionalized polyolefins. These modified polyolefins are described in U.S. Patent Nos. 6,001,484 and 6,072,003, which are incorporated herein by reference. Other useful agents include modified
30 rubbers.

B. Modified Polyolefin

The term "modified polyolefin" means a random, block, or graft olefin copolymer having in a main or side chain thereof a functional group such as carboxylic acid; C₁ to C₈ carboxylate ester such as carbomethoxy, carboethoxy,

carbopropoxy, carbobutoxy, carbopentoxo, carbohexoxy, carboheptoxy, carboctoxy, and isomeric forms thereof; carboxylic acid anhydride; carboxylate salts formed from the neutralization of carboxylic acid group(s) with metal ions from Groups I, II, III, IV-A and VII of the periodic table, illustratively including sodium, potassium, lithium, magnesium, calcium, iron, nickel, zinc, and aluminum, and mixtures thereof; amide; epoxy; hydroxy; amino; C₂ to C₆ acyloxy such as acetoxo, propionyloxy, butyryloxy; and the like; wherein said functional group is part of an unsaturated monomer precursor which is either copolymerized with an olefin monomer or grafted onto a polyolefin to form said modified polyolefin.

The modified polyolefin component defined above is represented by a large number of polyolefin random, block, and graft copolymers which have long been known in the art and, for the most part, are commercially available. Otherwise they are readily prepared using the conventional techniques for polymerizing olefin monomers; see Preparative Methods of Polymer Chemistry, W. R. Sorenson and T. W. Campbell, 1961, Interscience Publishers, New York, N.Y. Illustrative but non-limiting of the basic olefin monomers for copolymerization with the functional group containing unsaturated monomers are ethylene, propylene, butylene, mixtures of ethylene/propylene, mixtures of ethylene/butylene, mixtures of propylene/butylene, mixtures of ethylene/C₃ to C₁₂ α,β -unsaturated alkenes, and the like. Alternatively, the above illustrative monomers or mixtures are first polymerized to their corresponding polyolefins prior to grafting with said functional group containing monomers. A preferred class of modified polyolefin comprises a modified polyethylene, that is to say a polyethylene copolymer wherein the major molar proportion (at least 50 percent) of the copolymer consists of ethylene units copolymerized with at least one unsaturated monomer having a functional group substituent defined above, or a polyethylene (HDPE, LDPE or LLDPE) having grafted thereon a minor molar proportion (about 0.005 to 5 percent) of said at least one unsaturated monomer having the functional group substituent.

As illustrative embodiments of modified polyolefins in copolymer form are those derived from the copolymerization of any one of the olefin monomers set forth above but preferably ethylene in the minimum molar proportions of at least 50 percent with a vinyl functional group containing monomer such as acrylic acid,

methacrylic acid, maleic acid, maleic anhydride, acrylamide, methacrylamide, glycidyl acrylate, glycidyl methacrylate, vinyl acetate, vinyl butyrate, methyl acrylate, ethyl acrylate, butyl acrylate, 2-hydroxyethyl acrylate, sodium acrylate, zinc acrylate, the ionic hydrocarbon polymers from the polymerization of α -olefins with α,β -ethylenically unsaturated carboxylic acids as described in U.S. Pat. No. 3,264,272 the disclosure of which is incorporated herein by reference, and the like. It will be understood that in the case of the olefin/vinyl acid copolymers that the carboxylic acid groups can be wholly or partially converted to metal salts (*i.e.*, sodium, potassium, zinc) after formation of the copolymer. Such ionic copolymers are collectively recognized by the term "ionomers". The vinyl functional monomers can be used in combination. Furthermore, mixtures of any of these modified polyolefins can be used.

As illustrative embodiments of modified polyolefins in grafted form are those derived from the graft polymerization of any one of the vinyl functional group containing monomers set forth above (preferably maleic anhydride) onto any one of the olefin polymers set forth above but preferably polyethylene (HDPE, LDPE, LLDPE). The proportions of said graft monomers are preferably within the molar range of 0.005 to 5 percent set forth above. As with the copolymers above, mixtures or combinations can be employed. Further, the vinyl functional group containing monomers can be grafted onto the modified polyolefin copolymers discussed above. A preferred embodiment of such a polymer type includes the product obtained by grafting maleic acid or anhydride onto an ethylene/vinyl carboxylate copolymer or the saponified copolymer derived from ethylene/vinyl acetate. The graft copolymerization of the unsaturated carboxylic acid or its functional derivative or another functional group-containing vinyl monomer onto the olefin polymer can be conducted using various methods. For example, the olefin polymer, the graft monomer and a free-radical initiator are incorporated in a solution or suspension of the olefin polymer in a suitable solvent. It is also possible to conduct the graft copolymerization in the presence of the thermoplastic polyurethane elastomer, *i.e.*, after being blended with the thermoplastic polyurethane elastomer.

It will be understood by those skilled in the art that the modified polyolefins can be prepared using any combination of monomer reactants in either a copolymer, grafted copolymer, or copolymer-grafted copolymer configuration.

However, a most preferred class of modified polyolefin comprises a copolymer or graft copolymer of ethylene or polyethylene (particularly LDPE or LLDPE) with at least one vinyl monomer having a functional group selected from carboxylic acid, carboxylate salts, dicarboxylic acid or anhydride thereof, carboxylate ester, and acyloxy, and mixtures of said modified polyolefins. Particularly, preferred species of modified polyethylene in this class are ethylene/vinyl acetate copolymer, ethylene/ethylacrylate copolymer, ethylene/methacrylic acid copolymer, ethylene/acrylic acid copolymer, ethylene/maleic anhydride graft copolymer, maleic anhydride grafted ethylene/vinyl acetate copolymer, and mixtures thereof in any combination and proportions.

Another group of modified polyolefins which can be used in terms of the present invention either alone or in combination with the modified polyolefins mentioned above are styrene/ butadiene/styrene-block copolymer (SBS) and its hydrogenated form, *i.e.*, SEBS block-copolymer grafted with the functional grafting group mentioned above.

Specific examples of said grafted modified polyolefin are polypropylene or ethylene propylene rubber grafted with anhydride, acid or primary or secondary amine, ethylene acrylic acid copolymers.

The modified polyolefin should contain from about 0.01 to about 10 percent by weight (pbw) of the functional moiety based upon the weight of the entire polymer. More preferably, the polyolefin should contain from about 0.05 to about 5 pbw of the functional moiety, even more preferably from about 0.75 to about 2 pbw of the functional moiety, and still more preferably from about 0.15 to about 1.0 pbw of the functional moiety based upon the weight of the entire polymer.

Useful modified polyolefins can be obtained under the tradename POLYBOND™ 3000 (Crompton).

C. Modified Rubbers

Modified rubbers include homopolymer or copolymer rubbers that contain terminal or pendant moieties containing acid or anhydride groups (*e.g.*, carbonyl groups).

The terminal or pendent moieties typically derive from unsaturated carboxylic acids or unsaturated anhydrides. Examples of unsaturated carboxylic acids include citraconic acid, cinnamic acid, methacrylic acid, and itaconic acid.

Examples of unsaturated anhydrides include maleic anhydride, citraconic anhydride, and itaconic anhydride. The preferred terminal or pendent moieties are succinic anhydride groups, or the corresponding acid from a ring opening structure, that derives from maleic anhydride.

5 The functionalized rubbers should contain from about 0.01 to about 10 percent by weight (pbw) of the functional moiety based upon the weight of the entire polymer. More preferably, the functionalized rubbers should contain from about 0.05 to about 5 pbw of the functional moiety, even more preferably from about 0.75 to about 2 pbw of the functional moiety, and still more preferably from
10 about 0.15 to about 1.0 pbw of the functional moiety based upon the weight of the entire polymer.

The functionalized rubber additives are typically prepared by grafting unsaturated carboxylic acids or unsaturated anhydrides to a polyolefin polymer.

15 The techniques employed to attach the terminal or pendent moieties that contain carboxylic acid or anhydride groups to a polyolefin polymer are well known in the art. For example, grafting maleic anhydride to a polyolefin is disclosed in U.S. Patent No. 6,046,279, which is incorporated herein by reference.

20 The rubber to which the unsaturated carboxylic acids and hydrides are attached can include a variety of rubbers. In one preferred embodiment, the rubber is an ethylene propylene rubber (EPR) or an elastomeric copolymer such as a terpolymer of ethylene, propylene, and a diene monomer (EPDM). EPDM rubbers are well known and are described in U.S. Patent Nos. 6,433,090 and 6,437,030, which are incorporated herein by reference. Similar functionalized rubbers are disclosed in U.S. Patent No. 6,169,145, which is incorporated herein
25 by reference. Useful modified rubbers can be obtained under the tradename EXXELOR™ VA 1803 OR VA 1801 (ExxonMobil).

VII. Other Additives

30 Other additives that are typically employed in polymeric compositions can likewise be employed in practicing the present invention. These other additives can include pigments, UV stabilizers, biostats, fillers, oils, antioxidants, waxes, processing aids such as lubricants, and other similar ingredients.

VIII. Amounts

A. Thermoplastic Polyurethane

The polymeric blends of this invention will include from about 2 to about 30 percent by weight thermoplastic polyurethane, preferably from about 5 to about 20 percent by weight thermoplastic polyurethane, more preferably from about 7 to about 15 percent by weight thermoplastic polyurethane, even more preferably from about 9 to about 12 percent by weight thermoplastic polyurethane.

B. Copolyester

The polymeric blends of the present invention include from about 55 to about 145 parts by weight (pbw) copolyester per 100 parts by weight thermoplastic polyurethane (phr), preferably from about 70 to about 130 pbw copolyester phr, more preferably from about 80 to about 120 pbw copolyester phr, and even more preferably from about 90 to about 110 pbw copolyester phr.

C. EVA

The polymeric blends of the present invention include from about 400 to about 1,000 parts by weight (pbw) ethylene vinyl acetate copolymer per 100 parts by weight thermoplastic polyurethane (phr), preferably from about 500 to about 900 pbw ethylene vinyl acetate copolymer phr, more preferably from about 600 to about 800 pbw ethylene vinyl acetate copolymer phr, and even more preferably from about 650 to about 750 pbw ethylene vinyl acetate copolymer phr.

D. Softening Agents

In certain embodiments of this invention, the polymeric blends include from about 15 to about 85 pbw softening agent phr, preferably from about 30 to about 70 pbw softening agent phr, more preferably from about 40 to about 60 pbw softening agent phr, and even more preferably from about 45 to about 55 pbw softening agent phr.

E. Compatibilizing Agent

The polymeric blends of the present invention include from about 15 to about 85 pbw compatibilizing agent phr, preferably from about 30 to about 70 pbw compatibilizing agent phr, more preferably from about 40 to about 60 pbw compatibilizing agent phr, and even more preferably from about 45 to about 55 pbw compatibilizing agent phr.

IX. Preparation and Processing

The polymeric blends of this invention can be prepared by simply blending or mixing the polymeric ingredients together. Preferably, this blending

takes place at an elevated temperature, such as a temperature from about 150° to about 200°C, or preferably from about 160° to about 195°C. In an especially preferred embodiment, the polymeric blends are prepared by mixing the ingredients within a twin screw extruder that employs a high shear screw at a
5 temperature of about 180° to about 190°C.

X. Uses

The polymeric blends of this invention can be used in a number of applications. In one particularly embodiment, the polymeric blends can be
10 injection molded and adhered to a copolyester insert (*i.e.*, overmolded).

XI. Specific Embodiments

In one preferred embodiment, the polymeric blends of this invention include from about 6 to about 14, and more preferably from about 8 to about 12,
15 percent by weight thermoplastic polyurethane, from about 6 to about 14, and more preferably from about 8 to about 12, percent by weight copolyester, from about 55 to about 85, and more preferably from about 63 to about 77 percent by weight ethylene vinyl acetate, from about 2 to about 8, and more preferably from about 4 to about 6 percent by weight styrene-isoprene-styrene block copolymer, and from
20 about 2 to about 8, and more preferably from about 4 to about 6 percent by weight maleic anhydride modified polypropylene.

In one preferred embodiment, the polymeric blends of this invention include from about 6 to about 14, and more preferably from about 8 to about 12, percent by weight thermoplastic polyurethane, from about 6 to about 14, and more
25 preferably from about 8 to about 12, percent by weight copolyester, from about 55 to about 85, and more preferably from about 63 to about 77 percent by weight ethylene vinyl acetate, from about 2 to about 8, and more preferably from about 4 to about 6 percent by weight styrene-isoprene-styrene block copolymer, and from about 2 to about 8, and more preferably from about 4 to about 6 percent by weight
30 maleic anhydride modified EPDM.

Various modifications and alterations that do not depart from the scope and spirit of this invention will become apparent to those skilled in the art. This invention is not to be duly limited to the illustrative embodiments set forth herein.